Appl Nanosci (2014) 4:695–701
DOI 10.1007/s13204-013-0246-5

ORIGINAL ARTICLE

Energy band diagram of In: ZnO/p-Si structures deposited using chemical spray pyrolysis technique

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Received: 15 April 2013 / Accepted: 4 June 2013 / Published online: 18 June 2013

Abstract Near-ideal In: ZnO/p-Si heterojunction band edge lineup has been investigated with aid of I–V and C–V measurements. The heterojunction was manufactured by spray pyrolysis method of (Zn $(CH_3COO)_2 \cdot 2H_2O$) at different indium doping concentrations on monocrystalline p-type silicon. The experimental data of the conduction band offset ΔEc and valence band offset ΔEc were compared with theoretical values. The band offset $\Delta E\mathrm{c} = 0.45$ eV and $\Delta E\mathrm{v} = 1.65$ eV obtained at 300 K. The energy band diagram of In: ZnO/p-Si HJ was constructed. C–V measurements depict that the junction was an abrupt type and the built-in voltage was determined from C^{-2}–V plot.

Keywords Indium-doped ZnO · In: ZnO/p-Si heterojunction · Electronic properties · Chemical spray pyrolysis technique · Lineup

Introduction

Polycrystalline films have received a rapidly growing interest due to their increasing area of applications in advanced technologies for microelectronic, photonic, and micromachined devices. The heterostructures for photodetection and photovoltaic device applications were obtained using one of the following techniques, such as LPE, MOCVD, etc., which are very expensive for such applications. A good alternative low cost technology is based on the heterojunctions with transparent conducting oxide (TCO) thin film, such as In_2O_3, SnO_2 have been widely used for photovoltaic devices and recently ZnO having a direct optical band gap of 3.45 eV, a large melting point of 1,975 °C, a large exciton binding energy (60 meV), and a high transparency (>80 %) for visible light, which can be obtained with low resistivity (10^{-3} Ω cm), is playing an important role for optoelectronic applications (Purica et al. 2000; Singh et al. 2010; Ilican et al. 2008; Zhao et al. 2006; Škriniarová et al. 2008; Major et al. 1985). Transparent conductive ZnO films can be prepared by different methods, such as activated reactive or electron beam evaporation, magnetron- or electron beam-sputtering, spray pyrolysis, chemical vapor deposition with many variants, and recently by sol–gel technique (Ilican et al. 2008; Zhao et al. 2006). The structural, physical, and electrical properties of ZnO films were governed by deposition parameters and post-treatment (Mondal et al. 2008; Jeong et al. 2007; Kuo and Tuan 2007). To improve these properties can be doped with some elements. Especially, Group III elements, such as In^{3+}, Al^{3+}, Ga^{3+} are used to improve and/or control the electrical conductivity.

These dopants act as a donor when it occupies a substitutional position for Zn^{2+} cation or an interstitial position in the ZnO lattice. The efficiency of the dopant element related to its electronegativity and the ionic radius. Indium-doped ZnO films have been deposited different methods, such as sputtering, electrodeposition process, sol–gel deposition and spray pyrolysis. In this study, the films have been deposited by spray pyrolysis method. This method has variety advantages such as the low-cost, no-vacuum and easy doping. There have been extensive studies on the crystalline structure and optical transmittance of In-doped ZnO thin films prepared by spray pyrolysis method. However, there are not many reports on the study of indium dopant effect on electrical and electronical

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properties of In: ZnO/p-Si heterojunction device. In our previous works, we reported on ZnO and indium-doped ZnO films prepared by spray pyrolysis (Ilican et al. 2008). In addition, it has been found that the n-type doping of ZnO is relatively easy as compared to p-type doping. Group III elements like Al, Ga and In can be used as n-type dopant. Doping with Al, Ga and In has been attempted by many groups, resulting in high quality, highly conducting n-type ZnO thin films. Among group III element much of the work has been done using Al as a dopant because the ionic radius of Al is smaller than that of In and Ga (Singh et al. 2010; Afify et al. 2005).The heterostructure In: ZnO/p-Si is considered as anisotype heterojunction since In: ZnO behaves like n-type semiconductor. The junction capacitance (C) of the anisotype heterojunction of abrupt type can be expressed as (Shama et al. 1970):

$$C = \left[\frac{q\varepsilon_1\varepsilon_2 N_A N_D}{2(\varepsilon_1 N_A + \varepsilon_2 N_D)}\right]^{1/2} (V_D - V_a)^{-1/2} \quad (1)$$

where ε_1 and ε_2 are permittivity of narrow band gap and wide band gap, respectively, N_A and N_D are, respectively, the free carrier concentration of p-type and n-type semiconductors and V_a is the applied voltage.

Current transport mechanism of such heterojunction could be explained according to any of the diffusion model, the emission model, and the recombination model (Sharma and Purohit 1974; Sze 1981); a relation between J and V is represented by:

$$I \propto \exp\left(\frac{qV}{nKT}\right) \quad (2)$$

where q/kT is the reciprocal of volt equivalent of temperature and n is the diode factor.

The aim of this work is to obtain the electronic structure of the In: ZnO/p-Si heterojunction and study the effect of indium doping concentration on the electrical and electronical properties of the device.

Experimental work

Square-shaped p-type silicon samples, each of 1 × 1 cm^2 area, of 1.5–4 (Ω cm) resistivities were prepared using a wire-cut machine. Silicon wafers were washed ultrasonically in distilled water and were immersed in nitric acid HNO_3 for 3 min to remove ionic contamination. The wafers were immersed in HCl: HNO_3 (3:1) for 3 min to remove metallic films. They were etched in buffered hydrofluoric acid (34.6 % NH_4F: 6.8 % HF: 58.6 % H_2O) for 2 min to remove oxide films. The silicon wafers were cleaned in distilled water and dried in furnace at 130 °C. The resistivity and type of conductivity of the Si substrates were measured using 4-point probe technique. ZnO and IZO thin films were deposited on to (111) p-type mirror-like silicon substrates using the spray pyrolysis method. 0.2 M solution of Zn $(CH_3COO)_2 \cdot 2H_2O$ diluted in methanol and deionized water (3:1) was used for all the films. A magnetic stirrer is incorporated for this purpose for about 10–15 min to facilitate the complete dissolution of the solute in the solvent. Organic solvents are preferable over distilled water because the former enables the attainment of homogeneous, highly transparent, thin films of small grain size. For indium doping, $InCl_3$ was added to starting solution. The In/Zn ratio in the solution was 0, 2, 4 and 6 % (These films were named as ZnO, IZO_2 and IZO_4, respectively). The details of spray pyrolysis set-up are given in elsewhere (Singh et al. 2010). Chemical techniques for the preparation of thin films have been studied extensively because such processes facilitate the designing of materials on a molecular level. Spray pyrolysis, one of the chemical techniques applied to form a variety of thin films, results in good productivity from a simple apparatus. In the current research, zinc oxide thin films are deposited on silicon substrates employing locally made spray pyrolysis deposition chamber whose main components set-up is illustrated in the schematic diagram of Figs. (1, 2). It is essentially made up of a precursor solution, carrier gas

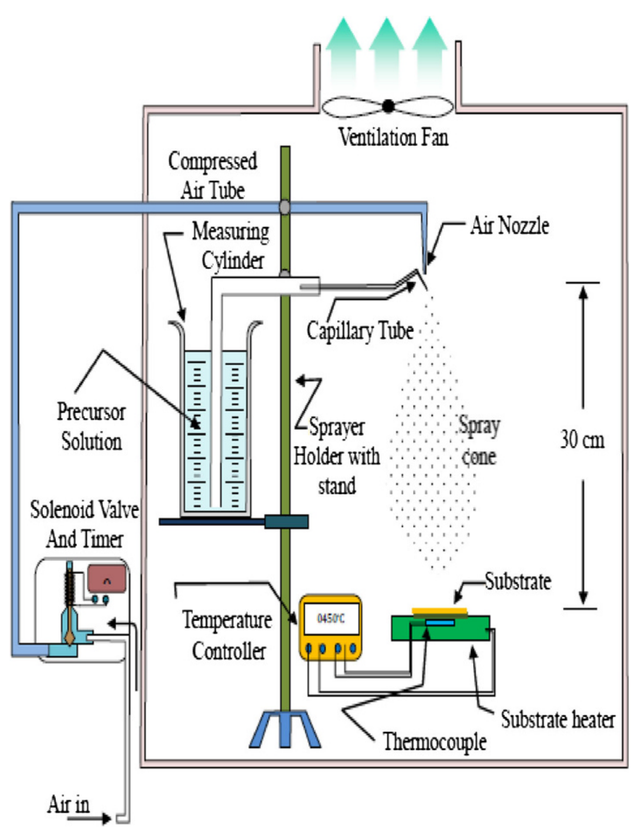

Fig. 1 Schematic set-up for spray Pyrolysis technique

Fig. 2 Photo plate. **a** Experimental set-up of the spray pyrolysis deposition SPD. **b** Air atomizer and **c** Gemo DT109 temperature controller

assembly connected to a spray nozzle, and a temperature-controlled hot plate heater.

The atomizer, illustrated in the photo plate (2-b), has an adjustable copper capillary tube nozzle of 0–0.8 mm inner diameter clamped to a holder and supported by a metal tripod. The nozzle is driven by a compressed atmospheric air. The prepared precursor solution is pumped through the metal nozzle with a solution flow rate ranging from 1 to 2 mL/min. Owing to the air pressure of the carrier gas; a vacuum is created at the tip of the nozzle to suck the solution from the tube after which the spray starts (Perednis and Gauckler 2005). To regulate spraying time, a 16-Bar Tork solenoid valve controlled by an adjustable timer has been incorporated. The atomizer and the 1,500 W hot plate heater are enclosed in a $1 \times 1 \times 1$ m^3 ventilation hood, photo plate (2-a). A 220 V a.c. power was applied to the heater and temperature was measured using a type K (nickel–chromium) thermocouple and precision digital temperature controller (GEMO DT109 photo plate (2-c)). The spray rate is usually in the range 2–3 mL min^{-1}. The optimum carrier gas pressure for this rate of solution flow is around 5 kg cm^{-2}. At lower pressures, the size of the solution droplets becomes large, which results in the presence of recognized spots on the films and then reduction of transparency. This situation increases the scattering of light from the surface and then reduces the transmittance of the films.

The spray pyrolytic substrate temperature is maintained within 450 ± 5 °C during the deposition. Film thickness is controlled by both the precursor concentration and the number of sprays, or alternatively, spraying time. Thus, a 4 s spray time is maintained during the experiment. The normalized distance between the spray nozzle and substrate was fixed at 30 cm. The film thicknesses were found to be approximately 150 nm. The silicon sample was used as substrate for TCO's/Si heterojunction. Ohmic contacts were fabricated by evaporating 99.999 purity aluminum wires for back and front contact using Edwards coating system, after contact and assembly processes I–V characteristic under different operating temperatures for In: ZnO/p-Si sample. C–V characteristics of the produced heterojunction were measured using a PM6306 programmable LRC meter supplied by Fluke at 1 MHz and reverse bias voltage ranged from 0.2 to 2.5 V. The cross point ($1/C^2 = 0$) of the ($1/C^2$–V) curve represents the built-in potential (V_{bi}) of the heterojunction (Sze 1981), the depletion layer width has been estimated using the following equation:

$$w = \sqrt{\frac{2\varepsilon_s V_D}{qN_d}} \tag{3}$$

The energy band diagram of In: ZnO/p-Si heterojunction was constructed theoretically depending on the experimental result, which is used in the analysis of the capacitance–voltage characteristics, photocurrent spectra, current voltage characteristics of photo- and dark conductivity and their temperature dependences. The Fermi level energy has been found using the following equation (Sppaval and Herman 1995):

$$\left.\begin{aligned} E_c - E_{fn} &= \frac{KT}{q}\ln\left(\frac{N_c}{N_d}\right) \\ E_{fp} - E_V &= \frac{KT}{q}\ln\left(\frac{N_V}{N_a}\right) \end{aligned}\right\} \tag{5}$$

The difference between the two conduction band energies is denoted by ΔE_C and the difference between the two valance band energies is denoted by ΔE_V.

$$\Delta E_c = x_n - x_p \tag{6}$$

$$\Delta E_v = \left(E_{g_n} - E_{g_p}\right) - \left(x_p - x_n\right) \tag{6}$$

and

$$\Delta E_c - \Delta E_v = E_{g_n} - E_{g_p} = \Delta E_g \tag{7}$$

E_{g_1} and E_{g_2} are the energy groups of narrow band and wide gap material, respectively.

On the other hand, current mechanism employs the emission model and its value is given in the following equation (Sharma and Purohit 1974):

$$I = A\exp\left[-\frac{q(\Delta E_c - V_D)}{KT}\right] \times \left[\exp\left(\frac{qV_a}{KT}\right) - 1\right] \tag{8}$$

where V_a is the applied bias, and $x_1 < x_2 < x_1 + E_{g_1}$ and $\varphi_1 > \varphi_2$. x_1, x_2 is the electron affinity for the two semiconductor materials, respectively.

The following figure explains the experimental set-up:

Results and discussion

Figure 3a, b gives the C–V and $1/C^2$–V measurements at different indium doping concentrations for In: ZnO/p-Si device, respectively. The results show that the device capacitance is inversely proportional to the bias voltage. The reduction in the device capacitance with bias voltage resulted from the expansion of depletion layer with the built-in potential. The depletion layer capacitance refers to the increment in charge per unit area to the increment change of the applied voltage. This properly gives an indication of the behavior of the charge transition from the donor to the acceptor region, which was found to be "abrupt" which is confirmed by the relation between $1/C^2$ and reverse bias being a straight line. The potential barrier at the junction can be measured by small-single capacitance–volt characteristic, since band bending is primarily on the Si side, the intercept of the curve on the x axis is essentially equal the diffusion potential within the silicon and it value is expected to depend on the Fermi level position in the conduction band at high carrier concentrations. The total value of the built-in voltage V_D can be calculated by extrapolating $1/C^2$–V plot to the point $1/C^2 = 0$. The intercept voltage V_{int} is related to the V_D by

$$V_D = V_{int} + (2kT) \tag{9}$$

where kT/q is the volt equivalent of temperature. The slope of the straight line gives the donor concentration, which its

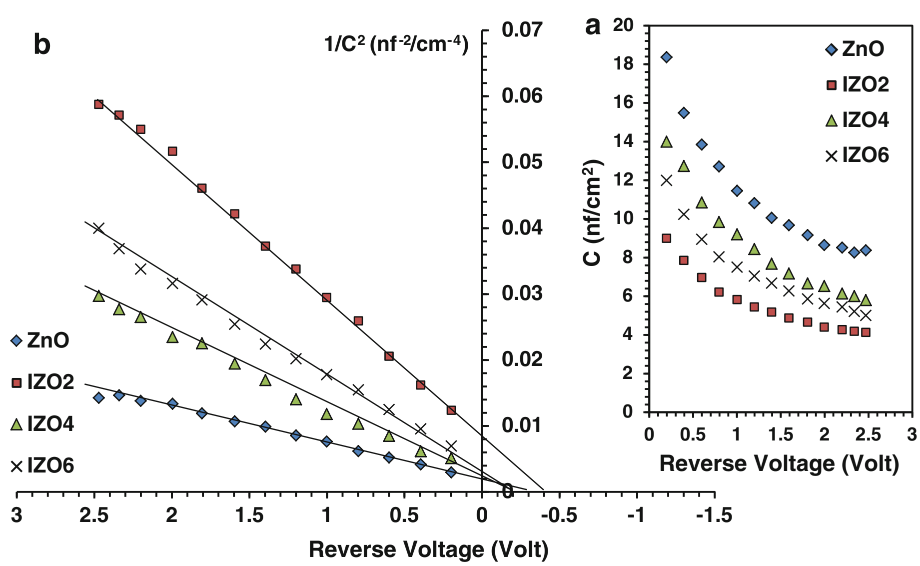

Fig. 3 **a** Junction capacitance as a function of the reverse voltage, **b** $1/C^2$ vs. reverse voltage for (In: ZnO/p-Si) device at different indium doping concentration

Table 1 The obtained results from the C–V measurements

In (%)	V_{bi} (V)	Nd (cm^{-3})	W (μm)	C (nF/cm^2)	Ec − Ef (eV)
0	0.3	2.8×10^{15}	0.34	26.02	0.23
2	0.4	0.7×10^{15}	0.79	11.20	0.26
4	0.2	1.4×10^{15}	0.39	22.69	0.24
6	0.25	1.0×10^{15}	0.52	17.01	0.25

value correspond well with the known resistivity of silicon substrate. The built in potential (V_{bi}), the width of the depletion layer (W) and the bulk Fermi level of p-type silicon substrate at different In doping concentrations are calculated and tabulated in the following (Table 1). It is observed the width of depletion layer (W) inversely proportional with built in potential and the optimum width value of the depletion layer found to be 0.79 at 2 % Indium doping concentration. A typical energy band profile of two isolated pieces of p-and n-type semiconductors and an equilibrium energy band profile of an abrupt p–n heterojunction formed by bringing in intimate contact two dissimilar semiconductors having the different type of conductivity. The In: ZnO exhibits n-type conductivity when it is prepared from p-type Si substrate, which has been experimentally, measured using 4-point probe devices. It is clear that the electron affinity of wide-band gap material (n-In: ZnO) (x_n) is higher than that of the substrate (p-Si) (x_p). The formation of a heterojunction with such forbidden gap of the two materials completely overlaps then this case is called staggered. In: ZnO/p-Si an isotype heterojunction, conduction is carried out almost entirely by electrons (the barrier to the transport of holes is much higher than the barrier seen by electrons) and the current will be given by the current equation of the emission model Eq. (2). The energy band profile of In: ZnO/p-Si an isotype heterojunction, depending on the electron affinities, work

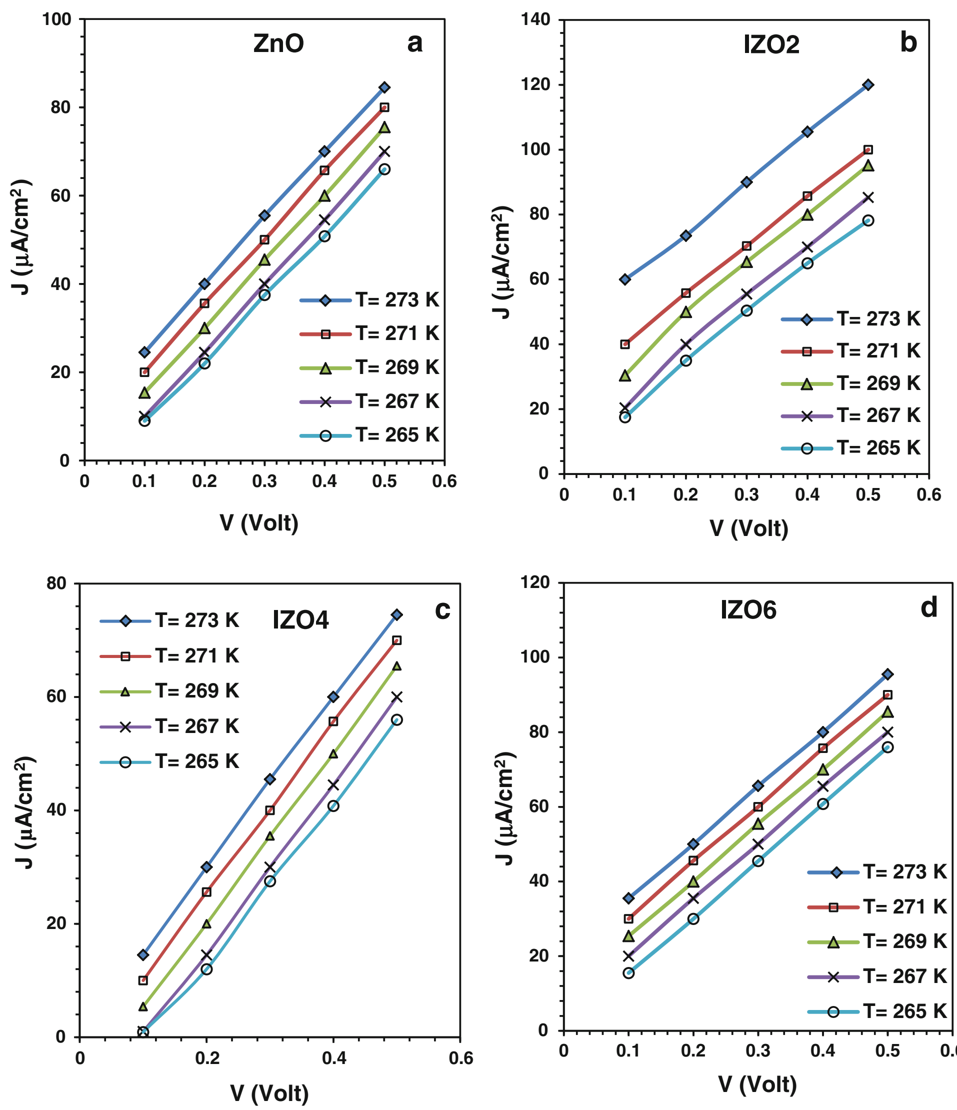

Fig. 4 **a–c** Current density at different cooling temperatures and at different In doping concentrations

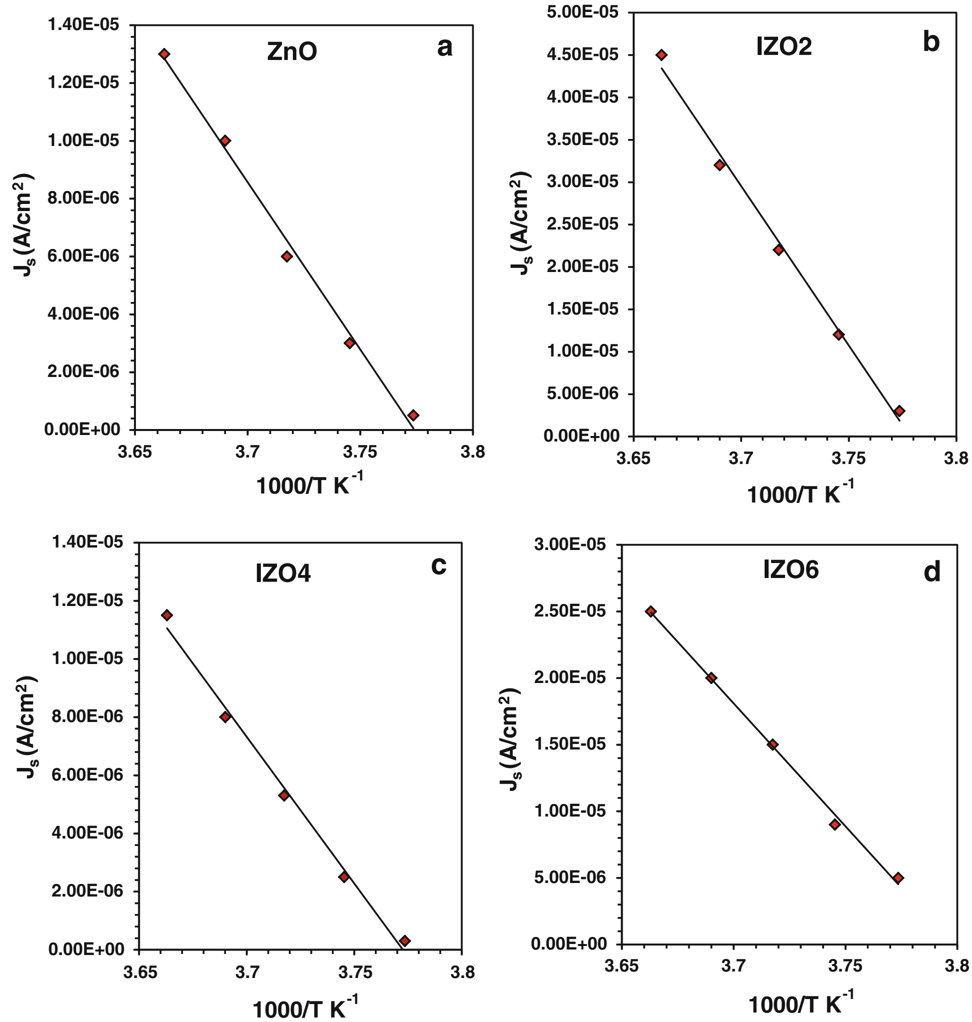

Fig. 5 a–c Saturated current density vs. 1,000/T and at different In doping concentrations

function and energy band gaps of semiconductors. Their necessary conditions and the current will be given by the current equation of the emission model. Figure 4a–d gives J–V characteristic at different cooling temperature at the range 273–265 K the extension of each curve led to J_s. Figures 5a–d, 6 gives the J_s (saturation current density) V_s 1,000/T for In: ZnO/p-Si device at different indium doping concentrations. The decrease in J leads to decrease in J_s. The slope of this plot can give the value of the conduction band of set ΔEc through Eq. (5). Neglecting interface parameters that are different to determine, the construction of the energy band diagram for (In: ZnO/p-Si) heterojunction can be estimated by determining ΔEv from Fig. 4c with aid of Eq. (6) depending on the value of ΔEc which has been found to be 0.45 eV and hence the value of ΔEv was found to be about 1.65 eV. This approximation has been used by many workers (Sharma and Purohit 1974). Barrier height (Φ_B) has been calculated for In: ZnO/p-Si device at 2 % indium doping concentration using Eq. 12, it has been found to be 0.61 eV of the (In: ZnO/p-Si) device (Sppaval and Herman 1995).

$$\Phi_B = KT/q \ln\left[A^* T^2/J_s\right] \quad (10)$$

where KT/q is the volt equivalent of temperature and J_s is the saturation current density.

Conclusions

Several conclusions can be drawn on the basis of obtained experimental data as shown below:

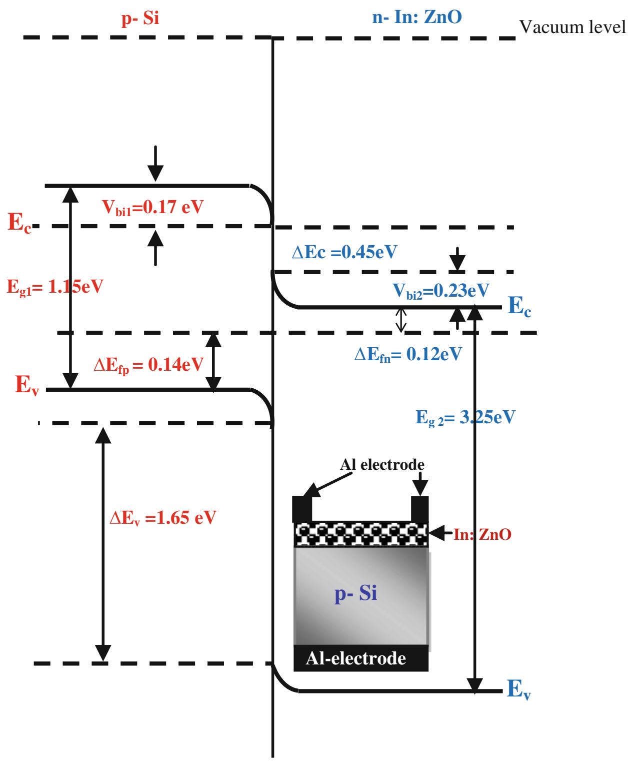

Fig. 6 Energy band diagram for n-In: ZnO/p-Si heterojunction device prepared at 2 % indium doping concentration

- The junction formed by spray pyrolysis of Zn $(CH_3COO)_2{\cdot}2H_2O$ at different indium doping concentrations on p-type Si is an isotype.
- C–V results suggest that the junction was abrupt type.
- Experimental value of ΔE_c seems to be consistent with the theoretically calculated ΔE_c with satisfactory accuracy.

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